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Phosphorus removal using ferric–calcium complex as precipitant: Parameters optimization and phosphorus-recycling potential

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HIGHLIGHTS

- A novel technology based on the complex of ferric and calcium salts was developed.
- The strongest synergistic effect was observed at Fe/Ca molar ratio of 7:3–4:1.
- The optimized parameters were: Fe/Ca = 2.4:1, A/P = 1.5:1, pH = 7, FMS = 100 rpm.
- The novel technology cut down the dosage by 36% compared with the traditional one.
- The novel technology increased the phosphorus (P_2O_5) content of precipitate to 30%.

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ABSTRACT

Pollution control and phosphorus recycling have become one of focuses in the field of wastewater treatment. Both the ferric and calcium salts are effective chemical reagents for the phosphorus removal from wastewater. Based on the complex of these two chemical reagents, a novel technology was developed. The results showed that ferric and calcium had an antagonistic effect at Fe/Ca molar ratio of 1:10–1:1, but a synergistic effect at Fe/Ca molar ratio of 1:1–10:1. The strongest synergistic effect was observed at Fe/Ca molar ratio of 7:3–4:1. When the wastewater with concentration of 100 mg P/L was treated using the ferric–calcium complex as precipitant, the optimized parameters were: Fe/Ca = 2.4:1, ferric–calcium complex/phosphorous (A/P) = 1.5:1, pH = 7, fast mixing speed (FMS) = 100 rpm. Compared with the traditional technology using ferric salt as sole precipitant, the phosphorus removal technology using ferric–calcium complex cut down the dosage by 35.53%, leading to a low cost of $ 3.69/kg P; and it increased the phosphorus (P_2O_5) content of precipitate up to 29.77%, indicating a good potential for recycling. The phosphorus removal technology using ferric–calcium complex as precipitant provides a prospective alternative for the removal and recycling of phosphorus in wastewaters.

1. Introduction

The world is facing a threat of eutrophication nowadays. Phosphorus is one of the major factors that cause eutrophication [1–3]. As reported by Carpenter et al. [4], a water body would take on eutrophication when the total phosphorus concentration exceeded 0.015 mg/L. The concentration of phosphorus in different wastewater varies from several milligrams per liter (domestic wastewater) to a few hundred milligrams per liter (livestock wastewater) and even up to tens of thousands milligrams per liter (industrial wastewater). Since a large amount of phosphorus originates from wastewaters, the removal of phosphorus from wastewaters has become an indispensable measure to control eutrophication.

On the other hand, phosphorus is a finite resource on the Earth [5,6], and it may be depleted over the next 100 years [7–9]. The analysis by the authors in Fig. 1 [9], indicated 2033 as the peak year for phosphorus production. According to previous research [10], globally 21.4 Mt elemental phosphorus from rock phosphate was consumed of which 6.1 Mt can technologically be recycled from waterways and wastewater in 2009. So, it is of great importance to recycle phosphorus from wastewater. The development of efficient technology for phosphorus removal and recovery will promote both the control of water pollution and the recycling of phosphorus resource.

Currently, phosphorus removal technologies mainly include chemical, biological and bio-chemical methods [11–13]. Among them, chemical technology is widely used to achieve low residual phosphorus concentrations so as to meet the discharge standard. Ferric and calcium salts are two popular precipitants for phosphorus

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removal. Phosphorus removal using ferric salt is an efficient method, but it has some drawbacks such as high treatment cost, low effluent pH and difficult recycling of phosphorus from precipitates [14,15]. In contrast, phosphorus removal using calcium salt is a cost-effective option for phosphorus recycling from precipitates, but it leads to an unacceptably high effluent pH of over 10 [16,17]. Based on the properties of two precipitants, the phosphorus removal using ferric–calcium complex was hypothesized to be a good technology. The objective of this work is to set up a novel technology for phosphorus removal and recycling; to optimize the parameters of the technology using ferric–calcium complex and to observe the recycling potential of produced precipitates.

2. Experimental methods

The operational conditions influencing the phosphorus removal process were investigated in laboratory experiments. Batch tests were carried out with synthetic wastewater. Synthetic wastewater was prepared with deionized water and stock solutions. Stock solution of dipotassium hydrogen orthophosphate (KH_2PO_4) was prepared from solid reagent (AR, Yonghua Chemical Technology (Jiangsu) Co., Ltd) with concentration of 10.0 g P/L. The concentration of working phosphate solution was 100 mg P/L. The concentrations of precipitants (calcium hydroxide ($Ca(OH)_2$, AR, Sinopharm Chemical Reagent Co., Ltd.) and ferric sulfate ($Fe_2(SO_4)_3$, AR, Xilong Chemical Co., Ltd.)) were 22.0 g Ca/L and 20.1 g Fe/L respectively which were directly used so as not to dilute the reaction system.

All experiments were performed in 250 mL glass beakers using mechanical stirrers to homogenize the contents. With intensive stirring in the tests (examining the effects of Fe/Ca, dose, pH, fast mixing speed (FMS)), precipitants were added to 250 mL beakers containing 150 mL synthetic wastewater. The Fe/Ca ratio was set according to the reaction equation. The reactions are shown below.

$$\mathrm{Fe}^{3+} + 3\mathrm{OH}^- = \mathrm{Fe(OH)}_3(\mathrm{s}) \quad \Delta_r G_m(T, \mathrm{Fe(III)}) = -124.92\ \mathrm{kJ\ mol}^{-1}$$

$$5\mathrm{Ca}^{2+} + 7\mathrm{OH}^- + 3\mathrm{H_2PO_4^-} = \mathrm{Ca_5(OH)(PO_4)_3} \quad \Delta_r G_m(T, \mathrm{Ca(II)}) = -319.06\ \mathrm{kJ\ mol}^{-1}$$

The mixing intensity was tested by initial fast mixing for 1 min, then gentle mixing (at 50 r/min) for 15 min, and finally settling for 30 min. The pH value of reaction solution was regulated beforehand using sodium hydroxide (NaOH, 1 mol/L, Hangzhou Xiaoshan Chemical Reagent Co., Ltd) or hydrochloric acid (HCl, 1 mol/L) and it was no longer regulated during or after reaction. All tests were run in triplicate. The supernatant was taken to determine the residual phosphorus concentration. The precipitate was centrifuged at 7000 r/min for 5 min and dried at 70 °C for 10 h.

Phosphate was determined according to the ascorbic acid photometric method, with a detection limit of 10 μg P/L. The precipitate structure was observed by scanning electron microscope (SEM, Ultra 55 field emission scanning electron microscope, the German Corlzeis D company) and the elemental component was analyzed by energy dispersive X-ray spectroscopy (EDS, X-ray spectrometer EDS7429). At the sample surface, three points were chosen to determine elemental contents. The elemental contents of phosphorus were estimated using P (wt%) and P_2O_5 (wt%, Eq. (2.1)) where, $M_{P_2O_5}$ (142 g/mol) and M_p (31 g/mol) are the formula weight of P_2O_5 and phosphorus, respectively

$$P_2O_5 = M_{P_2O_5}/2M_p \times P = 2.29P \qquad (2.1)$$

3. Results and discussion

3.1. Effects of operation parameters on phosphorus removal

3.1.1. Effect of Fe/Ca molar ratio

To determine the appropriate Fe/Ca molar ratio, batch tests were conducted to investigate the effect of Fe/Ca molar ratio on the phosphorus removal. Other conditions were: concentration = 100 mg P/L, A/P = 1, pH = 7, FMS = 200 rpm. The precipitants were added to remove equivalent amount of phosphorus stoichiometrically. For instance, Fe/Ca = 4 meant that 0.8 mol ferric salt and 0.33 mol calcium salt were added to precipitate altogether 1 mol phosphorus. If the molar phosphorus removal using ferric–calcium complex as precipitant is higher than the sum using ferric and calcium salts, it is defined as synergistic effect. On the contrary, if the molar phosphorus removal using ferric–calcium complex as precipitant is less than the sum using ferric and calcium salts, it is defined as antagonistic effect. Using ferric and calcium salts respectively, the molar phosphorus removal was 60.88% and 54.65% in the experiments. So, their average 57.76% was taken as the critical value to judge synergistic or antagonistic effect. According to the data shown in Fig. 2, the effect of ferric–calcium complex on the phosphorus removal was antagonistic when the proportion of ferric salt in the ferric–cal-

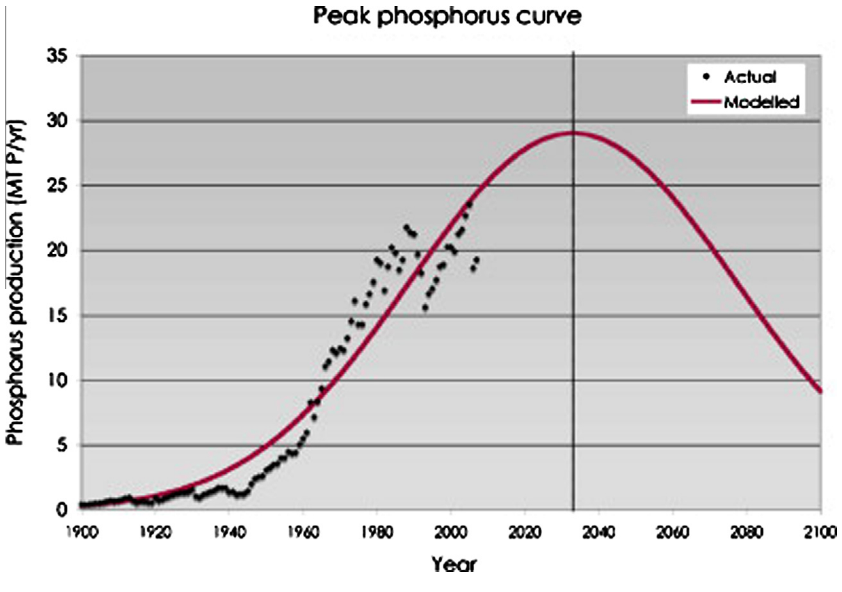

Fig. 1. Peak phosphorus curve indicating a peak in production by 2033, derived from US Geological Survey and industry data. Source: [9].